Asian Journal of Chemistry Vol. 17, No. 4 (2005), 2657–2662

Synthesis and Spectral Studies of Some Novel Oxovanadium(IV) Complexes of 2,3-Dimethyl-1-Phenyl-4-(2-hydroxy-5-chlorophenylazo)pyrazol-5-one

SALI THOMAS† and M.L. HARIKUMARAN NAIR*
Department of Chemistry, University College, Thiruvananthapuram-695 034, India
E-mail: salipanackal@yahoo.com

Some novel oxovanadium(IV) complexes of the ligand 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-chlorophenylazo) pyrazol-5-one (chlorophenolazoantipyrine, CPAAP) with the composition $VO(CPAAP)X_2$ (where X = ½ SO_4, NO_3, Cl, Br, I, NCS or ClO_4) have been prepared and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, IR, electronic, ^1H NMR and ESR spectral studies. The ligand and one of its complexes were screened for their antibacterial activity against gram-positive and gram-negative bacteria. The ligand behaves as neutral bidentate in all the complexes. All the complexes show normal magnetic behaviour. The complexes are found to be monomeric and neutral with square pyramidal geometry.

Key Words: Synthesis, Oxovanadium(IV), Chlorophenolazoantipyrine, Square pyramidal.

INTRODUCTION

The chemistry of oxocations has been very interesting because the metal-oxygen multiple bond in them could be used as an internal molecular probe to understand more about the nature of the metal-ligand bonds as the M—L bonds perturb the more sensitive M═O bonds[1]. Oxovanadium(IV) is one of the most stable and well established oxometal species[2]. The good affinity of this species towards tridentate ONO donor ligands is the principal cause for its rich chemistry with such donor atoms. Complexes with such donor atoms are mainly with Schiff bases, but those with azo ligands have received only little attention. In view of this, it was thought of interest to investigate the coordinating ability of an ONO donor azo ligand derived from 4-aminoantipyrine, *viz.*, 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-chlorophenylazo)pyrazol-5-one (chlorophenolazoantipyrine, CPAAP) towards VO(IV). The present report includes the preparation and characterisation of a few VO(IV) complexes of CPAAP.

---

†Department of Chemistry, All Saints, College, Thiruvananthapuram-695 007, India.

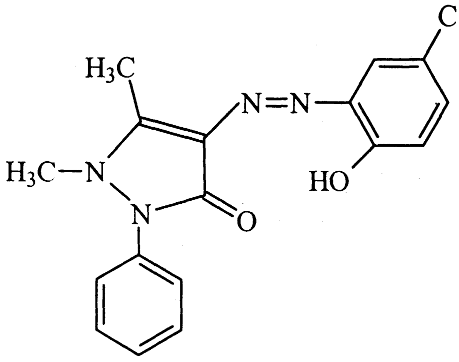


Fig. 1. Chlorophenolazoantipyrine (CPAAP)

EXPERIMENTAL

Oxovanadium(IV) sulphate ($VOSO_4 \cdot 5H_2O$), 4-aminoantipyrine (Fluka, Switzerland) and *p*-chlorophenol (Spectrochem, Mumbai) were used as supplied. The oxovanadium(IV) nitrate, chloride, bromide, iodide, perchlorate and thiocyanate were prepared from the sulphate salt. All other chemicals used were of AR grade.

The ligand CPAAP was prepared as in literature[3]. About 10 g (50 mmol) of 4-aminoantipyrine in 28 mL of 1 : 1 HCl was diazotized and the resulting diazonium salt solution was added slowly with stirring to an ice-cold alkaline solution of *p*-chlorophenol (6.4 g, 50 mmol). The mixture was kept in an ice-bath for 30 min with occasional stirring. The reddish brown solid product separated was suction filtered, washed with water and recrystallized from alcohol (m.p. 208°C).

Complexes were prepared by refluxing methanolic solutions of the respective vanadyl salt and the ligand in 1 : 1 molar ratio for 5–6 h. The solid complex obtained by volume reduction was filtered, washed with aqueous methanol followed by benzene and dried over P_4O_{10} *in vacuo*.

Vanadium in the complexes (except in perchlorate) was estimated as V_2O_5 by ignition[4]. As the perchlorate complex exploded on heating, the metal was estimated by peaceful pyrolysis method[5]. Chloride and bromide were estimated by Volhard's method[4]. Iodide was estimated gravimetrically as silver iodide, while sulphate and thiocyanate as barium sulphate[4]. Perchlorate was estimated by Kurz's method[6]. Room temperature magnetic susceptibilities of the complexes were measured in Gouy balance, calibrated using $Hg[Co(NCS)_4]$. Molar conductances in nitrobenzene, methanol and acetonitrile were measured using an Elico bridge type CM 82T with a dip type cell having platinum electrodes (cell constant 0.94 cm^{-1}). The electronic (in methanol), infrared (in KBr) and ^1H NMR (in $CDCl_3$) spectra were recorded on a JASCO V-550 UV-Vis, Perkin-Elmer 397 and 300 MHz (Bruker Avance dpx-300) FT-NMR (using TMS as reference) spectrophotometers, respectively. The ESR spectrum of one of the complexes in polycrystalline form at room temperature was recorded on a Varian E-112 X-Q band spectrometer with DPPH as reference material. The antibacterial activity of the ligand and one of its complexes at different concentrations were tested by disc diffusion method using two bacteria, *viz.*, *Staphylococcus aureus* and *Escherichia coli.*

RESULTS AND DISCUSSION

All the complexes are stable, crystalline and non-hygroscopic. They are soluble in methanol and ethanol but insoluble in benzene and ether. Analytical data are in agreement with the compositions proposed for the complexes as in Table-1. The electrical conductances of the complexes in nitrobenzene, acetonitrile and methanol are consistent with their non-electrolytic nature. The room temperature magnetic moments of the complexes (Table-1) are close to the spin-only value for a d^1 system indicating the absence of any metal-metal interaction[7].

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF OXOVANADIUM(IV) COMPLEXES

Complex (Colour)	Found (Calculated) (%)					Molar conductance (ohm^{-1} cm^2 mol^{-1})*			μ_{eff} (B.M.)
	Metal	S/Cl	C	H	N	$C_6H_5NO_2$	CH_3OH	CH_3CN	
$[VO(CPAAP)SO_4]$	9.97	6.28	40.12	2.95	10.99	2.3	21.4	26.3	1.74
(Brown)	(10.07)	(6.33)	(40.36)	(2.97)	(11.08)				
$[VO(CPAAP)(NO_3)_2]$	9.45		38.06	2.79	15.63	3.3	23.2	25.2	1.77
(Brown)	(9.54)		(38.25)	(2.81)	(15.75)				
$[VO(CPAAP)Cl_2]$	10.49	14.63	42.23	3.09	11.56	3.1	25.3	36.3	1.76
(Brown)	(10.60)	(14.78)	(42.46)	(3.12)	(11.66)				
$[VO(CPAAP)Br_2]$	8.86		35.64	2.62	9.78	2.9	23.1	28.9	1.75
(Brown)	(8.95)		(35.85)	(2.64)	(9.84)				
$[VO(CPAAP)I_2]$	7.59		30.56	2.24	8.38	4.8	26.2	32.5	1.74
(Dark brown)	(7.67)		(30.75)	(2.26)	(8.44)				
$[VO(CPAAP)(NCS)_2]$	9.61	12.07	43.22	2.83	15.88	3.7	24.6	30.4	1.76
(Dark brown)	(9.69)	(12.18)	(43.40)	(2.85)	(15.99)				
$[VO(CPAAP)(ClO_4)_2]$	8.28	11.56				4.9	32.3	43.6	1.75
(Dark brown)	(8.37)	(11.67)							

*$\times 10^{-3}$

The ^1H NMR spectrum[8] of the ligand shows two singlets corresponding to the methyl protons observed at δ 2.7 and δ 3.27. The latter may be due to the N-methyl protons. The signal due to the five aromatic protons of the antipyrine phenyl ring appeared as a multiplet between δ 7.46–7.55 and that due to the protons of the phenol ring is observed as a multiplet between δ 6.8–7.3. The signal due to the phenolic —OH proton appeared at δ 8.29.

The IR spectrum of the ligand exhibits a broad band of medium intensity at 3100 cm^{-1} assignable to hydrogen bonded —OH group[9]. This band is absent in the spectra of all the complexes and a new broad band of medium intensity appears *ca.* 3400 cm^{-1}, indicating the presence of free —OH group. The ν(C=O) occurring at 1660 cm^{-1} in the ligand spectrum shows a red shift to *ca.* 1600 cm^{-1}. Similarly, the ν(N=N) observed at 1450 cm^{-1} in the spectrum of the ligand is also red shifted to *ca.* 1420 cm^{-1}. These observations indicate the coordination of the carbonyl and azo groups to the metal ion. The non-ligand bands around 550 and 470 cm^{-1}, assignable to ν(V—N) and ν(V—O) respectively, support the coordination through azo group nitrogen and carbonyl oxygen atoms[10]. Thus, the IR spectra reveal the neutral bidentate coordination of CPAAP in all the complexes.

IR spectrum of the sulphate complex shows the presence of coordinated sulphate group. The bands at 1218, 1170 and 1050 cm^{-1} (split components of ν_3), 990 cm^{-1} (ν_1), 648, 616 and 585 cm^{-1} (split components of ν_4) and at 456 cm^{-1} (ν_2) is characteristic of the bidentate chelating nature of sulphate group[11]. The bands at 1475 (ν_4) and 1350 cm^{-1} (ν_1) with a separation of 125 cm^{-1} in the spectra of the nitrate complex are suggestive of monodentately coordinated nitrate group[12, 13]. The N-coordinated nature[14] of the thiocyanate group is indicated by the spectral bands at 2044 ν(C—N), 830 ν(C—S) and 490 cm^{-1} δ(N—C—S). The additional bands in the spectra of the perchlorate complex at 1120, 1030, 930, 640 and 610 cm^{-1} are assignable to ν_4, ν_1, ν_2, ν_3 and ν_5 vibrational modes of unidentately coordinated perchlorate group[15]. A very strong band observed at *ca.* 980 cm^{-1} in the spectra of all the complexes may be assigned to V=O streching frequency[16].

The electronic spectra of the complexes show three bands in the region 12500–12270 cm^{-1}, 15400–14800 cm^{-1} and 22730–21700 cm^{-1} assignable to $d_{xy} \rightarrow d_{xz}, d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions respectively. The number and positions of the bands are consistent with a square pyramidal arrangement around the metal ion[17].

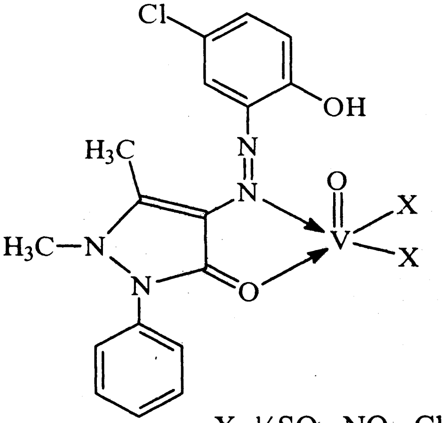
The polycrystalline X-band ESR spectrum of the complex [VO(CPAAP)SO_4] is anisotropic and hyperfine splitting is observed in both parallel and perpendicular components. The g and A values calculated are $g_\perp = 1.92$, $g_\parallel = 1.75$, $g_{av} = 1.806$, $A_\parallel = 128.5G$ and $A_\perp = 142.8G$. The observed trend $g_\perp > g_{av} > g_\parallel$ in the complex indicates that the unpaired electron is present in the d_{xy} orbital of the V(IV) atom[18].

The antimicrobial activityies of the ligand and the complex [VO(CPAAP)$(NCS)_2$] were tested against gram positive bacteria *Staphylococcus aureus* and gram negative bacteria *Escherichia coli* by disc diffusion method at different concentrations using gentamicin as positive control[19] and absolute methanol as negative control. The samples were dissolved in absolute methanol and impregnated in Whatmann no. 1 filter paper discs. The methanol in the discs was evaporated and the discs were sterilized by autoclaving. Muller Hinton agar plates were inoculated with the test bacterial strains. The test and control sample discs were placed on the media surface and incubated at 35°C for 24 h. After incubation, the diameter of the zone of inhibition was measured. The test results (Table-2) show that the ligand and the complex do not exhibit any antibacterial activity towards *Staphylococcus aureus* and *Escherichia coli* in the concentrations studied.

TABLE-2
TEST RESULTS OF ANTIBACTERIAL ACTIVITY OF CPAAP AND $[VO(CPAAP)(NCS)_2]$

Complex/Ligand	Zone of inhibition (µg/disc)			
	S. aureus		*E. coli*	
CPAAP	20	Nil	20	Nil
	40	Nil	40	Nil
	80	Nil	80	Nil
	160	Nil	160	Nil
$[VO(CPAAP)(NCS)_2]$	20	Nil	20	Nil
	40	Nil	40	Nil
	80	Nil	80	Nil
	160	Nil	160	Nil

On the basis of the above physicochemical studies, the complexes may be formulated as $[VO(CPAAP)X_2]$ where X = ½SO_4, NO_3, Cl, Br, I, NCS or ClO_4 and a square pyramidal geometry can be suggested for all the complexes (Fig. 2).



X=½SO_4, NO_3, Cl, Br, I, NCS or ClO_4

Fig. 2.

REFERENCES

1. J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).
2. R.J.H. Clark, The Chemistry of Titanium and Vanadium, Elsevier, London (1968).
3. A.I. Vogel, A Text Book of Practical Organic Chemistry, 3rd Edn., ELBS (1973).
4. ———, A Text Book of Quantitative Inorganic Analysis, 3rd Edn., John Wiley, New York (1963).
5. M.R. Gopalakrishnan Nair, M.J. Kurian and C.P. Prabhakaran, *Talanta*, **28**, 395 (1981).
6. E. Kurz, G. Kober and M. Berl, *Anal. Chem.*, **30**, 1983 (1958).
7. T.R. Rao, M. Sahay and R.C. Aggarwal, *Indian J. Chem.*, **24A**, 244 (1985).

8. D. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, 4th Edn., Tata McGraw-Hill, New Delhi (1988).
9. K. Ueno and A.E. Martell, *J. Phys. Chem.*, **60**, 1270 (1956).
10. J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York (1971).
11. K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, Wiley- Interscience, New York (1978).
12. B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091 (1961).
13. C.C. Addison, N. Logan, S.C. Wallwork and C.D. Barner, *Quart Rev.*, **25**, 289 (1971).
14. A. Sabatini and I. Bertini, *Inorg. Chem.*, **5**, 204 (1960).
15. D.K. Koppikar, P.V. Sivapulliaiah, L. Ramakrishnan and S. Soundararajan, *Structure and Bonding*, **34**, 135 (1978).
16. M.R. Gopalakrishnan and C.P. Prabhakaran, *Indian J. Chem.*, **24A**, 345 (1985).
17. C.J. Ballhausen, B.F. Djurinskij and K.J. Watson, *J. Am. Chem. Soc.*, **90**, 3305 (1968).
18. B. Singh, B.P. Yadava and R.C. Aggarwal, *Indian J. Chem.*, **23A**, 575 (1984).
19. C.H. Collins and P.M. Lync, Microbiological Methods, Butterworth, London (1970).

(*Received*: 20 January 2005; *Accepted*: 25 July 2005) AJC-4306